Chapter Three

Plant Sources of Lecithin

Phospholipids are functioning phosphatides of cell membranes and organelles that interact with metabolites, ions, hormones and antibodies. The mixture mainly consists of lecithin, cephalin and a group of minor polar lipids and glycolipids (Fig. 3-1) (1-5). The terms lecithin and phosphatidylcholine are often used interchangeably. Though the word lecithin is derived from the Greek term lekithos meaning "yolk of an egg", the primary commercial source of lecithin is plant seed. Food manufacturers use the term "commercial lecithin" to denote emulsifiers and wetting agents prepared during vegetable oil refining. Vegetable oil production produces phosphatides as by-products. The 1988 USDA forecast for world production of major oilseed, the sources of vegetable oils, shows production at 204.8 million metric tons for 1987/88 (6-9); world production of oils is 52.1 million metric tons for 1987/88. The ranking of the major oilseeds are soybean, cottonseed, peanut, sunflower seed, rapeseed, copra, flax seed, palm kernel, and sesame seed. In 1983, 75,000 metric tons of lecithin were available worldwide, mainly from soybean oil, and about 45% of that was manufactured and used in the U.S. (10). Commercial lecithin, due to its multifunctionality and wide applicability, sells for 2-10 times the price of soybean oil. Weihrauch and Son (11) present a concise review of phospholipid composition in various foods. A recent study by Smiles *et al.* (12) shows the effect of degumming reagents on the composition and quality of recovered lecithin from selected oilseed. Lecithin is widely used in manufactured food, feed and pharmaceutical, cosmetic and industrial applications such as crystal formation, and anti-dusting, modifying, emulsifying, dispersing, wetting, penetrating and antioxidizing agents (4, 12-16).

Soybean Lecithin

Soybean lecithin, obtained as a by-product of oil processing, is mainly

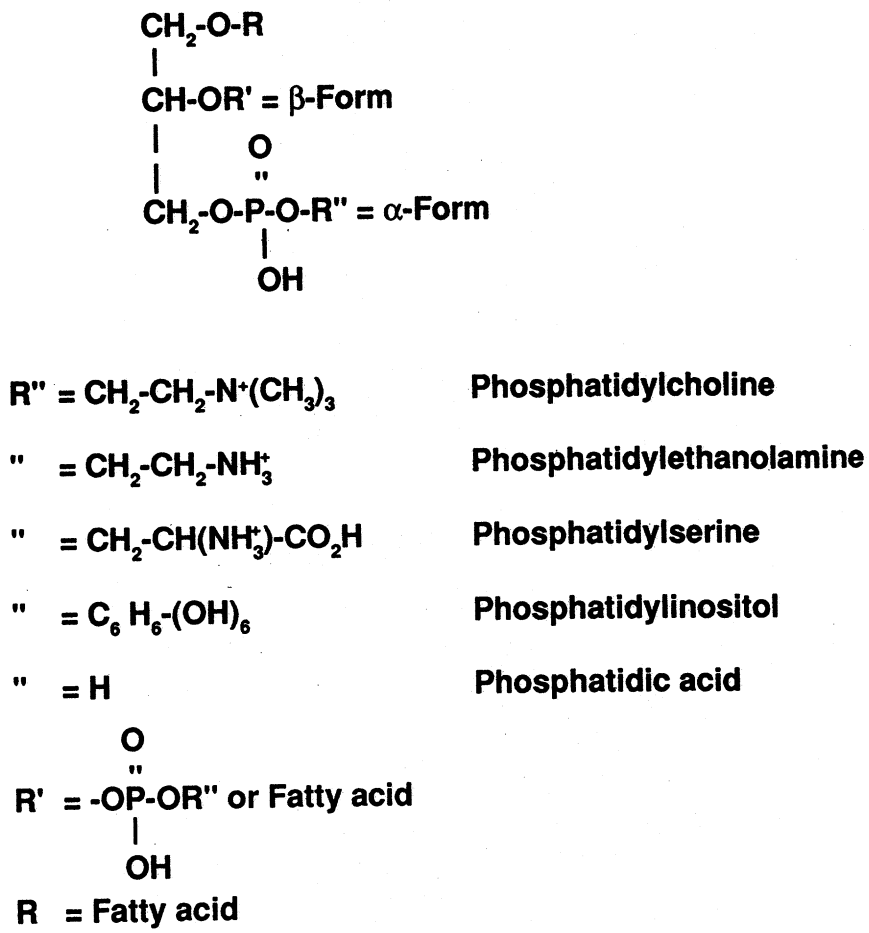


Fig. 3-1. Some phospholipids in plants.

used because of its availability and excellent properties, especially emulsifying behavior, color and taste (Fig. 3-2) (1). After dehulling, flaking and cooking the oilseed, the oil is removed by one of four methods: hydraulic pressing, screw pressing, prepress solvent extraction, or direct solvent extraction. Prior to degumming, the crude oil is filtered to remove meal fines. Then, the phospholipids are hydrated by thoroughly mixing the crude oil with a controlled amount of water and heat; sludge is removed by centrifugation and dried. Soybean phospholipids (2.3% of the crude oil) form the principal components of the sludge. Precise

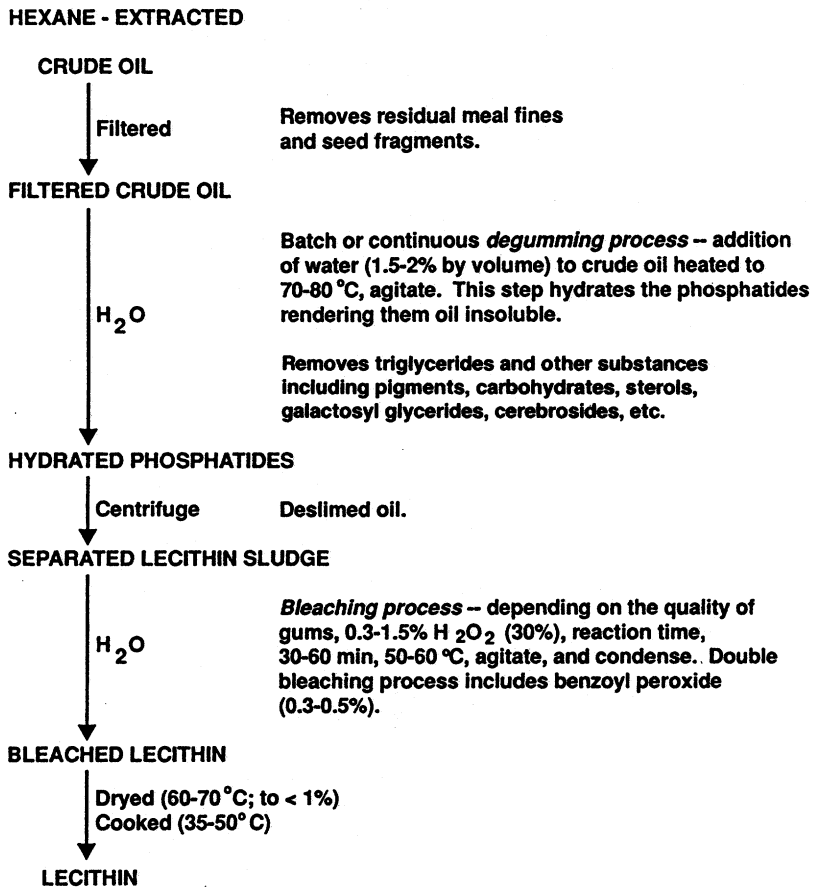


Fig. 3-2. Processing of soybean lecithin.

processing controls are necessary to produce a good quality, light-colored product that can be stored for months without significant change in quality.

A wide range of data is published showing much variability in the composition of phospholipids and fatty acids in lecithin (Tables 3-1 and 3-2) (1, 11-14, 17-18). The source of this variability may be genetic (plant cultivar/variety grown), seed quality (maturity, harvesting-caused damage, and handling/storage conditions), oil processing variables, or accuracy of detection and quantitative techniques. Lecithin is a by-product of oil processing; as a result, purification steps used to pro-

TABLE 3-1

Components (%) of Soybean Lecithin

Component	Range of Composition		
	Low	Intermediate	High
Phosphatidylcholine	12.0-21.0	29.0-39.0	41.0-46.0
Phosphatidylethanolamine	8.0-9.5	20.0-26.3	31.0-34.0
Phosphatidylinositol	1.7-7.0	13.0-17.5	19.0-21.0
Phosphatidic acid	0.2-1.5	5.0-9.0	14.0
Phosphatidylserine	0.2	5.9-6.3	——
Lysophosphatidylcholine	1.5	8.5	——
Lysophosphatidylinositol	0.4-1.8	——	——
Lysophosphatidylserine	1.0	——	——
Lysophosphatidic acid	1.0	——	——
Phytoglycolipids	——	14.3-15.4	29.6

TABLE 3-2

Fatty Acids (%) of Soybean Lecithin

Fatty acid	Range of Composition		
	Low	Intermediate	High
Myristic (C14:0)	0.3-1.9	——	——
Palmitic (C16:0)	11.7-18.9	21.5-26.7	42.7
Palmitoleic (C16:1)	7.0-8.6	——	——
Stearic (C18:0)	3.7-4.3	9.3-11.7	——
Oleic (C18:1)	6.8-9.8	17.0-25.1	39.4
Linoleic (C18:2)	17.1-20.0	37.0-40.0	55.0-60.8
Linolenic (C18:3)	1.6	4.0-6.2	9.2
Arachidic (C20:0)	1.4-2.3	——	——

duce a quality oil may be detrimental to lecithin components. Soybeans exposed to frost or subjected to prolonged storage periods have reduced lecithin yields (1). Phospholipases which produce phosphatidic acids from phospholipids reducing the yield of lecithin are active during these periods (19). The high chlorophyll content of immature soybeans is difficult to remove by traditional bleaching methods (20-21). Phospholipid content changes during the development of the soybean from 51.5%

at nine days after flowering to 8.1-10.2% at 55 and 97 days of growth (22). During the maturation process, the major phospholipids (phosphatidylcholine, phosphatidylethanolamine and phosphatidylinositol) increase while others decrease or remain constant.

Further purification of crude phospholipids is completed when their use requires a neutral flavor, light color or absence of oil. Colored pigments include carotenoids, chlorophylls and pheophytins (1, 21). Other constituents include tocopherol, biotin, folic acid, thiamin, riboflavin, panothenic acid, pyridoxine and niacin (5, 20). Through gas chromatography and mass spectroscopy, 79 volatile compounds were identified in soybean lecithin (20). Several of the compounds may be autooxidative decomposition products of unsaturated fatty acids of phospholipids responsible for the undesirable flavor of oil-free soybean lecithin. Extraction with acetone removes the oil, and to some extent, the pigments. Simple bleaching with hydrogen peroxide or a double bleaching by adding benzoyl peroxide improves color. Depending on the type of use, purified phospholipids can be dissolved in refined oil or processed into a powder or granulated form.

Each phospholipid contributes to the functionality of lecithin (13-16). Therefore, the data in Tables 3-1 and 3-2 suggest the potential for lecithin sources selected with varying functional properties. Where variability is genetically related, this potential is greatly heightened. Seed sources with high amounts of selected phospholipids can be used for extraction of these components. Also noted are the minor components which, with further study, may be shown to contribute to new and unique applications.

Modification of the phospholipids by various means can change their physicochemical characteristics, and in turn, their emulsifying, stabilizing and dispersing properties (1, 13-14, 23-24). For example, fractionation of the phospholipids in ethanol changes the ratio of phosphatidylcholine to phosphatidylethanolamine to produce products with improved emulsifying and anti-spattering properties; partial hydrolysis by phospholipase A, acid, or alkali produces products with improved hydrophilic and emulsifying properties; acetylation of phosphatidylethanolamine improves emulsifying properties; and hydroxylation improves emulsifying properties and water dispersibility.

Cottonseed Lecithin

During the 1930-40s, limited quantities of cottonseed phospholipids were commercially available (3-4, 25). Most of the phospholipids were in

the non-oil materials (1.0-2.0%) separated from hydraulically pressed oil by alkali or water washing. Different extraction methods normally used in the oil crushing industry cause few differences in the percentages of phospholipids or fatty acids in cottonseed oil. Table 3-3 lists the major phospholipids and fatty acid compositions of cottonseed lecithin (3-4, 25). Limited data are available in the literature on the composition of all cottonseed phospholipids. Scientists have not individually separated and quantified all of the lecithin and cephalin components.

TABLE 3-3
Composition (%) of Cottonseed Lecithin

Component	Extract	Phosphatidylcholine	Phosphatidylethanolamine	Phosphatidylserine
Phospholipids	1.8-2.2	34.9-35.9	13.7-20.1	7.0-26.0
Fatty acids:				
Myristic (C14:0)	0.4	0.3	0.4	0.6
Palmitic (C16:0)	32.9	31.1	33.7	33.3
Palmitoleic (C16:1)	0.5	0.3	0.3	0.6
Stearic (C18:0)	2.7	2.8	2.2	0.3
Oleic (C18:1)	13.6	11.5	11.5	14.4
Linoleic (C18:2)	50.0	54.0	49.0	50.4
Total gossypol	9.13	2.34	22.43	19.90
Free gossypol	0.02	2.24	0.05	0.01

Extraction and analysis methods contribute major qualitative and quantitative variations to comparative evaluations. The published literature contains a diversity of standard research procedures for isolating the total phospholipid portion of plant materials (4, 26-33). They include solvent extraction of the lipids and application of various separation and purification steps to the extract to fractionate and quantitate the individual phospholipids. Additionally, these procedures have steps to concentrate the crude phospholipid extracts, remove nonphospholipid impurities, and selectively precipitate or extract the phospholipids. These methods use solvent, solvent-solvent countercurrent, fractionation, metal salt complexing and precipitation, column chromatography separations and fractional crystallization procedures. Thin layer gas liquid and quantitative or preparative high performance liquid chromatographic procedures are used to separate, identify, and quantify small quantities of phospholipids as well as monitor other separation

procedures. Clearly, a selection of the right combination of solvent systems and detection techniques is an art in phospholipid research.

Most cottonseed grown for commercial use have gossypol-containing glands (3-4, 25). Cottonseed products or blends containing gossypol intended for human use in the United States must contain no more than 0.45% free gossypol. The dark-brown color caused by gossypol in cottonseed meal, oil, and lecithin also limits their use in foods. For gossypol-containing glanded cottonseed, the heat and moisture of the old hydraulic press method of oil extraction caused the pigment to bind to constituents in the meal rather than those in the oil. Changes in oil extraction processes have produced oils which contain considerable amounts of free gossypol pigments that bind to crude phospholipids and cause color and toxicity problems. The ultraviolet spectrum of the total phospholipid extract and fractionation studies shows that gossypol in the lecithin fraction is mainly present in a bound form with phosphatidylethanolamine and phosphatidylserine (Table 3-3). The very complex molecular components formed include monophosphatidylethanolamine-monogossypol, monophosphatidylserine-monogossypol, diphosphatidylethanolamine-monogossypol, diphosphatidylserine-monogossypol, and monophosphatidylethanolamine-monophosphatidylserine-monogossypol.

Cotton cultivars that produce glandless or gossypol-free cottonseed now provide potential sources of commercial food grade oil, lecithin or phospholipids, as well as meals and flours that are free of gossypol (3-4, 25). Glandless cottonseed is processed much more efficiently than glanded cottonseed and produces higher quality edible kernels, oil and protein products. Furthermore, kernels and meal fines can be flaked and extracted with hexane to produce quality oil and defatted meal. With glandless cottonseed, the need for expensive heat treatment during processing to bind gossypol in the phospholipid and meal fractions is eliminated. Also, a refined oil from glandless cottonseed requires less purification, reducing the loss of neutral oil and lecithin. The advent of glandless cottonseed presents an opportunity to make food-grade phospholipids as by-products of edible oil production.

All major cottonseed phospholipids are contained in the lecithin as follows: phosphatidylinositol (13.4% of total phosphorus), phosphatidylserine (2.4), phosphatidic acid (8.8), phosphatidylcholine (23.2), and phosphatidylethanolamine (13.5) (3-4, 22, 25, 29). Since cottonseed oil and lecithin have only trace amounts of fatty acids with more than two double bonds (linolenic acid), it is stable to oxidation and rancidity. Other sources of phospholipids (e.g., soybean) contain linolenic acid in

amounts that can affect flavor, color and odor. With the potential for increasing revenues, decreasing waste disposal costs, and reducing emulsion problems, glandless cottonseed oil and lecithin products become economically attractive.

Total phospholipid composition of seed from different cotton cultivars showed little variation (3-4, 22, 25). Some varietal variations were noted for unsaturated fatty acids, especially in the total phospholipid fraction. Thus, the potential exists for selected breeding of fatty acid composition in cottonseed phospholipids. Like soybean, the phospholipid composition of five- and ten-day cottonseed was high. Between 15 and 60 days, the composition dropped significantly. The individual phospholipids in the cephalin fraction varied during maturation; only phosphatidylethanolamine decreased to a lower amount at 60 days compared to 5 days. The percentage of total saturated fatty acids in cottonseed phospholipids, especially palmitic acid, decreased to approximately one-third the initial value during the 60-day growing period. However, the unsaturated fatty acids, oleic and linoleic acids increased. As noted for soybeans, genetic variability exists for phospholipid composition in cottonseed, and the highest quality lecithin is obtained from sound, minimally damaged and matured seed.

Corn Lecithin

Patents for commercial preparations of corn phosphatides and for products containing lecithin (cosmetics, ointments, foaming agents and rust inhibitors) were issued during the 1930-1950s (19, 34-35). The growth in demand for corn sweeteners may make other products of the corn-refining industry, such as lecithin, more available and competitive. Tables 3-4 and 3-5 illustrate the distribution of polar lipids and fatty acids in lecithin of corn compared to soybean (19, 34-35). Similar compositions were noted for the major phospholipids of phosphatidylcholine, phosphatidylinositol and phosphatidic acid. Glycolipids represent a higher proportion of polar lipids in corn than in soybean lecithin. The percentages of minor components, sterylglycoside ester and other glycolipids, are more than twice that of soybean. Both the glycolipids and phospholipids of corn have lower percentages of linolenic acid and are more saturated than those of soybean. Linoleic acid varies from 42-70% depending on the variety of corn. This genotypic effect on fatty acid composition of phospholipids introduces the possibility that lecithin with selected content of these nutritional components can be obtained by corn breeding.

TABLE 3-4

Distribution (%) of Polar Lipids in Corn and Soybean Lecithin

Polar lipid	Corn	Soybean
Sterylglycoside ester	15.0	4.3
Monogalactosyldiglyceride	1.8	0.8
Digalactosyldiglyceride	3.7	3.0
Other glycolipids	9.8	6.4
N-acyl phosphatidylethanolamine	2.6	2.2
N-acyl lysophosphatidylethanolamine	3.7	10.4
Phosphatidylethanolamine	3.2	14.1
Phosphatidylglycerol	1.4	1.0
Phosphatidylcholine	30.4	33.0
Phosphatidylinositol	16.3	16.8
Phosphatidic acid	9.4	6.4
Phosphatidylserine	1.0	0.4
Lysophosphatidylethanolamine	trace	0.2
Lysophosphatidylcholine	1.7	0.9

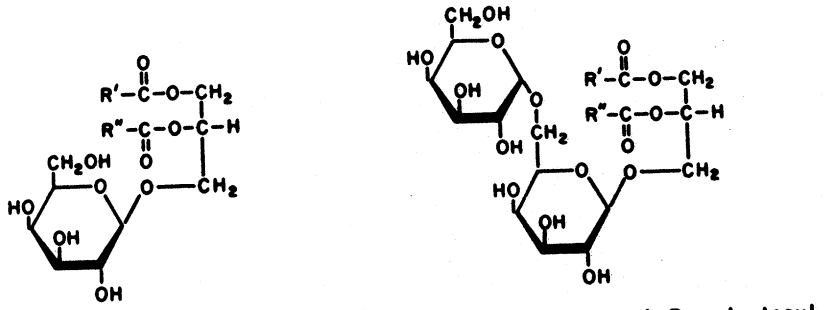
TABLE 3-5

Fatty Acid Composition (%) of Corn and Soybean Lecithin

	Composition	
Fatty acid	Corn	Soybean
Palmitic (C16:0)	17.7	17.4
Stearic (C18:0)	1.8	4.0
Oleic (C18:1)	25.3	17.7
Linoleic (C18:2)	54.2	54.0
Linolenic (C18:3)	1.0	6.8

Phytic acid, 88% of which is in the corn germ, is extracted as part of the lecithin fraction (19, 34). Elimination of phytate in corn lecithin is desirable because it binds zinc, magnesium and calcium. This binding decreases the nutritional availability of these important minerals. The functionality, particularly the emulsifying properties of corn lecithin, may differ from those of soybean lecithin due to the higher proportion of the minor components, e.g., glycolipids to phospholipids in the former mixture. Glycolipids, e.g., mono- and digalactosyldiglycerides, play an

important role in breadmaking properties (Figs. 3-3 and 3-4) (36–38). The lower level of linolenic acid in corn lecithin is an advantage over that of soybean since this triunsaturated fatty acid oxidizes readily to produce off-flavors. Corn has approximately one-tenth of the phospholipase D activity of soybean (19).



1,2-Diacyl-3-β-D-galactosyl-sn-glycerol (Monogalactosyldiglyceride)

1,2-Diacyl-3-[6-α-D-galactosyl β-D-galactosyl]-sn-glycerol (Digalactosyldiglyceride)

Fig. 3-3. Structural formulas of glycolipids.

Types of Bonds Detected between Glycolipids and Wheat-Flour Macromolecules

Method of Study	Glycolipid-Starch	Glycolipid-Gliadin	Glycolipid-Glutenin
Solvent extraction of gluten proteins	—	Hydrogen	Hydrophobic
Lipid binding in starch dough	Hydrogen	—	—
Infrared spectroscopy	Hydrogen	Van der Waals, hydrogen	Van der Waals, hydrogen
Nuclear magnetic resonance spectroscopy	Hydrogen, some induced dipole interaction	—	Hydrophobic and hydrogen
Audoradiography	Strong interaction in bread	—	Interaction in dough
Baking test	Hydrophobic and hydrogen bonds are essential for improvement in bread making.		

New Sources of Plant Lecithins

In response to the needs of food scientists, technologists and nutritionists, researchers are compiling data on phospholipids and their fatty acids from new seed sources (10-11, 25, 29-30, 36-37, 39-52). Oilseed and cereal grains continue to be identified as good sources of phospholipids. In India, the gummy materials containing valuable phosphatides, which presently are lost in the soapstock when crude ricebran oil is refined, have potential to be upgraded to commercial lecithin for useful food and non-food applications (42). Leafy vegetables, fruiting parts, roots and tubers are, with few exceptions, relatively poor dietary sources of total lipids and phospholipids. Nonconventional seeds are being considered because their constituents have unique chemical properties and may augment the supply of edible oils. The study of minor constituents, such as phospholipids, in these seeds is important for their effective use.

Potential sources of phospholipids include Canola/rapeseed, sunflower seed, peanut, palm kernel, xenophytic cucurbit seed, cereal grains including wheat, barley, and rice, and olive, mango and avocado fruit. Nonconventional sources include palash (*Butea monosperma*), papaya (*Carica papaya*), jangli bodani (*Sterculia factida*), coriander (*Coriandrum sativum*) and carrot (*Daucus carota*) seed. Phosphatidylcholine, phosphatidylethanolamine and phosphatidylinositol have been identified as major components in all of these sources (Table 3-6) (10-11, 25, 29-30, 36-37, 39-52). Minor components include lysophosphatidylcholine, lysophosphatidylethanolamine, phosphatidic acid, phosphatidylglycerol, glycolipids and triglycerides. Differences were noted among minor phospholipids which could alter the functionality of lecithin derived from these seed sources. Canola lecithin was shown to contain a greater amount of glycolipids than sunflower and soybean lecithin.

The predominant fatty acids present in the total and individual phospholipids of these sources were oleic, linoleic and palmitic acids (Table 3-7) (10-11, 25, 29-30, 36-37, 39-52). In general, except for differences in linolenic acid composition, data for the major phospholipids and fatty acids were similar to soybean lecithin. Smiles *et al.* (11), for example, noted that Canola phospholipids were lowest in palmitic, stearic and linoleic acids and contained the highest levels of oleic acid when compared to those of soybean and sunflower. Oils high in the monounsaturated fat, oleic acid, have been suggested to reduce blood cholesterol levels (53). Canola oil has been shown to have one of highest contents

TABLE 3-6
Phospholipids (%) of Selected Plant Sources

	Phospholipids		
Source	Phosphatidylcholine	Phosphatidylethanolamine	Phosphatidylinositol
Rapeseed	16:2; 20.0-24.6	15.0-17.5; 22.1	7.6-8.0; 14.7-18.0
Sunflower seed	12.7-26.8; 42.2-64.2	9.9-29.4; 46.6	3.7-21.4; 24.0-36.6
Peanut seed	49.0	16.0	22.0
Cucurbit seed	55.8-74.9	10.5-18.7	13.7-17.2
Rice bran	20.4-23.1	17.8-20.2	5.8-6.6
Barley seed	44.3-44.4	7.6-8.8	1.1-1.3
Olive fruit	47.3-58.9	5.3-8.0	18.0-23.9
Avocado fruit	37.0-44.9	12.0-19.5	12.1-18.0
Palash seed	44.6	14.8	27.0
Jangli badam seed	30.0	23.0	40.6
Papaya seed	28.1	18.7	34.0
Coriander seed	44.0	29.3	23.1
Carrot seed	29.1	35.4	23.1

TABLE 3-7

Fatty Acids (%) of Phospholipids from Plant Sources

Source	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Rapeseed	18.3-21.7	0.6-1.1	22.3-23.1	38.0-47.9	7.4-9.4
Sunflower seed	11.1-31.9	3.0-7.9	13.3-17.3	42.8-68.7	—
Peanut seed	12.9-33.9	2.6-2.8	30.9-47.0	27.5-35.6	—
Cucurbit seed	21.4-22.5	5.2-6.5	13.0-18.8	37.4-50.0	—
Rice bran	18.1	4.0	42.8	33.6	1.5
Barley seed	26.2	6.2	17.2	42.0	2.6
Olive fruit	18.0-21.2	4.8-5.3	51.9-65.6	9.4-15.5	1.4-4.0
Avocado fruit	17.8-26.4	1.9-2.0	35.4-46.0	23.6-26.0	4.0-4.5
Palash seed	26.5	3.6	33.2	35.4	—
Jangli badam seed	38.3	4.8	16.9	23.8	1.6
Papaya seed	24.4	6.9	61.4	7.0	—
Coriander seed	19.1	0.9	44.7	34.4	0.9
Carrot seed	24.3	1.8	26.2	42.4	5.5

(10%) of the polyunsaturated fat, α-linolenic acid, an omega-3 essential fatty acid (9, 54). Its linoleic acid content (22%) is relatively low. In comparison, soybean has a high content of both α-linolenic (7%) and linolenic (54%) acids. Other vegetable oils studied have trace amounts of α-linolenic acid.

Genetic variability was noted in studies of phospholipid content in three species of xenophytic cucurbits, *Cucurbita digitata* Gray, *C. foetidissima HBK* and *Apodonthera undulata* Gray (41). A study of heritability of fatty acid compostion of *C. foetidissima* seed oil revealed wide variability (55); this variation may also occur in the phospholipid fraction.

Depending on the processing method (moisture, heat, expelled versus solvent extracted, solvent type, etc.) used, analyses of phospholipid composition can produce results that vary greatly among plant sources. For instance, solvent-extracted oils contain the highest levels of phosphorus. The type of treatment of the oil to remove water and triglycerides affects phospholipid composition. Levels of minor components normally associated with the oil, such as sterols, tocopherols, pigments, phytic acid, carbohydrates, metal ions, etc., influence the refining techniques used and, therefore, the amount and quality of the final product.

As an example, rapeseed lecithin is obtained by the traditional water degumming process (39). Although rapeseed lecithin's composition is similar to that of soybean, it is considered inferior in color, flavor, taste and general appearance. Consequently, its use in the food industry has been limited. At the crushing plant, the gums removed from the rapeseed oil are added back to the meal, usually during desolventization. The addition of lecithin reduces the dustiness of the meal and increases its metabolic energy factor as livestock and poultry feed. In Europe, suitable refining treatments have been developed so that rapeseed lecithin can be utilized in margarine and chocolate. The development of low-erucic rapeseed cultivars, or Canola, has further advanced the use of rapeseed lecithin.

Plant lecithin is an invaluable ingredient in today's food, feed, cosmetic, pharmaceutical, wire manufacture, paint, automotive, construction, plastic molding, and magnetic media industries. Many chemists, food scientists and chemical engineers are developing new and improved processes for lecithin production. One excellent example of research utilizing lecithin demonstrates that wheat polar lipids, specifically mono- and digalactosyldiglycerides, play a significant role in breadmaking (Fig. 3-3) (36-38). It is thought that functionally these polar lipids interact with proteins and contribute to the volume of bread loaf (Fig. 3-4) (38). Despite lecithin's complex composition and varied sources, analyses have shown that the major phospholipids and fatty acids of lecithin are consistent with differences noted in proportions of phospholipids, minor constituents and fatty acid content. Two potentially important lecithin research areas lay ahead. They are the development of new or better sources of lecithin and the understanding of how lecithin contributes functional properties to and interacts with food, feed and other materials.

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